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Factors influencing atmospheric composition over subarctic North America during summer

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Elevated concentrations of hydrocarbons, CO, and nitrogen oxides were observed in extensive haze layers over northeastern Canada in the summer of 1990, during ABLE 3B. Halocarbon concentrations remained near background in most layers, indicating a source from biomass wildfires. Elevated concentrations of C_2Cl_4 provided a sensitive indicator for pollution from urban/industrial sources. Detailed analysis of regional budgets for CO and hydrocarbons indicates that biomass fires accounted for ≈ 70% of the input to the subarctic for most hydrocarbons and for acetone and more than 50% for CO. Regional sources for many species (including CO) exceeded chemical sinks during summer, and the boreal region provided a net source to midlatitudes. Interannual variations and long-term trends in atmospheric composition are sensitive to climatic change; a shift to warmer, drier conditions could increase the areas burned and thus the sources of many trace gases.

Introduction

Industrial and urban emissions provide massive inputs of pollutants to boreal and subarctic latitudes in winter and spring; rates for deposition and degradation are slow, and high pollutant concentrations are observed [*Rahn*, 1981; *Barrie et al.*, 1985; *Barrie*, 1986; *Stonehouse*, 1986; *Bottenheim et al.*, 1986; *Li and Winchester*, 1990]. Pollutant concentrations are much lower during summer [*Harriss et al.*, 1992]. Emissions from midlatitude sources appear to be efficiently scavenged during summer, and the influence of long-range transport is relatively weak. The composition of the atmosphere is most strongly affected by regional emissions, particularly boreal fires.

This paper summarizes observed concentrations of hydrocarbons, halocarbons, CO, and nitrogen oxides in the remote troposphere of subarctic central and eastern Canada in 1990, during the Arctic Boundary Layer Expedition (ABLE 3B). We use data for selected halocarbons and hydrocarbons to characterize emissions from urban/industrial sources and fires wildfires, providing information on emission ratios for key species on the regional scale. We quantitatively assess the relative contributions of these sources to regional budgets, using a photochemical model. Wildfires appear to provide a major source for these gases during summer, as suggested earlier by data from Alaska [*Blake et al.*, 1992; *Harriss et al.*, 1992; *Wofsy et al.*, 1992]. The subarctic is a net global source for many trace species, reversing the source-sink relationships observed in other seasons.

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Observations

Hydrocarbons and halocarbons (including C_2Cl_4) [*Blake et al.*, this issue] were determined in grab samples, 40 - 50 electropolished canisters filled on each 5-hour flight, and analyzed in the laboratory using gas chromatography. Sample acquisition required 30 - 60 s. Samples were preferentially acquired during vertical profiles and in haze layers. Other species were measured continuously on board, including CO (averaged into 10-s intervals [*Harris et al.*, this issue, *a*]) and NO_y and NO_x (averaged into 90-s intervals [*Sandholm et al.*, this issue). Samples for peroxyacetylnitrate (PAN) and acetone ($(CH_3)_2CO$) and a second determination of C_2Cl_4 were acquired over ≈60 s at ~2 min intervals and analyzed using an on-board gas chromatograph [*Singh et al.*, this issue].

Tetrachloroethylene represents a sensitive indicator for anthropogenic emissions. Its lifetime (~90 days in summer) is long enough to allow transport on a hemispheric scale but short enough to maintain a low background concentration. When air with elevated concentrations of CO and hydrocarbons was sampled, the anomaly could be attributed to long-range transport of pollution if concentrations of C_2Cl_4 were also elevated, and vice versa. Concentrations of C_2Cl_4 measured by the on-board chromatograph and in grab samples were in harmony at high concentrations (> 20 parts per trillion by volume (pptv)), but disagreed at low concentrations, reflecting different sampling times and possibly measurement and/or sampling artifacts. Correlations between C_2Cl_4, other halocarbons, and hydrocarbons were preserved in the grab samples at low concentrations, as shown in Figure 1, and we therefore focus on these measurements in our analysis.

Three areas were sampled extensively: Hudson Bay lowlands (HBL), Ontario (flights 4 - 9), central Labrador and Quebec LBQ), and eastern Labrador (ELO) with adjacent coastal areas (flights 11 - 20). These areas were selected to allow study of atmospheric composition for a range of biomes, dry and fire prone in HBL, somewhat wetter and cooler in LBQ and ELO, both remote from large urban complexes. Identifiable smoke plumes from large fires were sampled over HBL on flights 4, 6, 7, and 8. Industrial/urban pollution was sampled twice over Canada (flights 10 and 16) and over the East Coast of the United States (flights 21 and 22), providing a signature for urban/industrial emissions.

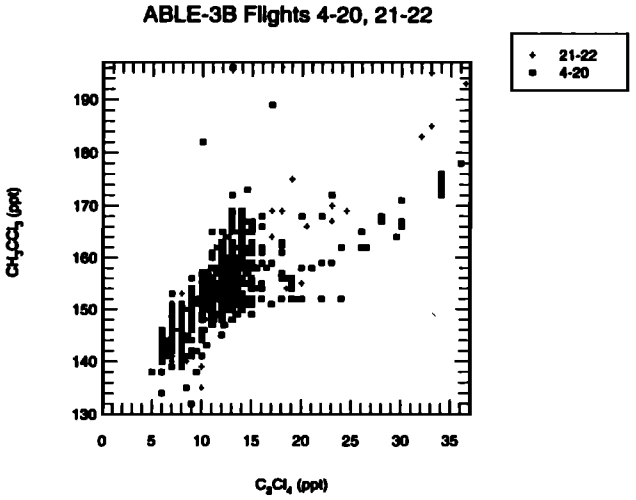

Fig. 1. Concentrations of C_2Cl_4 and CH_3CCl_3 observed in northeastern Canada (flights 4-20, squares) and over the East Coast of the United States (Maine - Virginia, flights 21 and 22, pluses).

Characteristic Urban/Industrial Emissions Ratioed Versus C_2Cl_4

Concentrations of C_2Cl_4 were steady, 11-12 ppt, for most flights. Lower values were observed in air with tropical character (e.g., anomalously low CO) on flights 14-16 [*Harriss et al.*, this issue, *b*]. Enhancements were observed simultaneously with elevated concentrations of other halocarbons and nonmethane hydrocarbons (NMHCs), as shown in Table 1, indicating urban/industrial pollution. Variance ratios were notably uniform relative to C_2Cl_4, within ±30% in most cases. Directly over source regions, ratios for CO:C_2Cl_4 were systematically lower, possibly reflecting incomplete oxidation of short-lived hydrocarbons that ultimately produce CO (see Figure 2).

Observations on flight 10 imply remarkably rapid advection of pollutants from midlatitude urban/industrial sources into the subarctic, confined largely within the planetary boundary layer (Figure 3). Variance ratios for pollutant species, relative to C_2Cl_4, were similar to observations over the source regions (flights 21 and 22; see Table 1), including species such as C_5H_{12} and NO_x, with lifetimes as short as ~5 days. According to *Bakwin et al.* [this issue], significant quantities of NO_x and other pollutants were transported to Schefferville (55°N) within the boundary layer during the summer of 1990. However, Table 1 shows that this mode of transport is inefficient for some species, for example for gases that deposit to the surface, such as NO_y or O_3, or that decompose at low altitudes, such as PAN. For example, variations of NO_y and PAN are either uncorrelated with C_2Cl_4 or variance ratios are inconsistent between U.S. and Canadian flights, reflecting the influence of surface deposition and atmospheric transformations.

Industrial/urban emissions north of 45° latitude, especially in Europe, are expected to contribute significantly to ambient concentrations of C_2Cl_4 and CO in subarctic Canada. Source inventories for Europe (including the former USSR) indicate

TABLE 1. Variance Ratios Relative to C_2Cl_4 (mol/mol)

Species	Mean Ratio (Pollution) α	Flight 21[a] Ratio	Flight 21[a] r^2	Flight 22[a] Ratio	Flight 22[a] r^2	Flight 16[b] Ratio	Flight 16[b] r^2	Flight 10[c] Ratio	Flight 10[c] r^2
CO[d]	3.80	2.96	0.45	4.09	0.77	8.90	0.63	3.80	0.87
C_2H_2	9.1	8.0	0.72	10.6	0.87	11.7	0.54	10.8	0.91
C_2H_6	31[e]	43.5	0.80	110.5	0.52	14.8	0.22	19.3	0.67
C_3H_8	10[e]	12	0.71	45	0.50	7.3	0.63	8.4	0.67
n–C_4H_{10}	3.7	2.3	0.86	4.6	0.62	3.7	0.73	4.2	0.67
i–C_4H_{10}	2.1	1.6	0.89	2.5	0.60	2.3	0.71	2.0	0.52
n–C_5H_{12}	1.6	1.2	0.93	1.5	0.46	2.0	0.69	1.9	0.85
C_6H_6	4.1	2.7	(0.22)	3.4	0.45	4.7	0.35	4.2	0.86
C_7H_8	2.1	-	note[f]	1.3	0.40	1.8	0.53	2.4	0.76
CH_4[d]	3.50	3.86	0.63	3.10	0.75	3.60	0.75	2.80	0.83
$(CH_3)_2C=O$	65	48	0.76	88	0.71	61	0.97	ND	
$CHCl_3$	0.14	0.14	0.70	0.11	0.75	0.18	0.78	0.14	0.8
CH_3CCl_3	1.7	1.91	0.87	1.49	0.51	1.32	0.88	1.28	0.83
CFC-113	0.29	0.29	0.60	0.20	(0.13)	0.16	0.46	0.41	0.54
CFC-11	0.50	0.87	0.46	-	note[f]	0.31	0.32	0.33	0.30
NO_y	41	25.6	0.50	57.0	0.62	15	(0.16)	-	note[f]
NO_x	4.3	6.2	0.73	3.5	0.39	-	note[f]	3.4	0.62
PAN		17.6	0.40	16.8	0.68	-	note[f]	-12.8	0.60

Units, mol/mol, except for CO and CH_4 which are 1000 mol/mol. Correlation coefficients (r^2) in parentheses are marginally significant, not used to compute means or medians. α, ratio to C_2Cl_4 used in Table 5.

[a]Data were selected to eliminate near-source values by rejecting concentrations of C_2Cl_4 > 25 ppt on flight 21, or altitudes < 2 km on flight 22.

[b]Marine boundary layer.

[c]Within 100 km of Schefferville.

[d]Units are mol/mol × 1000.

[e]Median value (see text).

[f]Insignificant correlation.

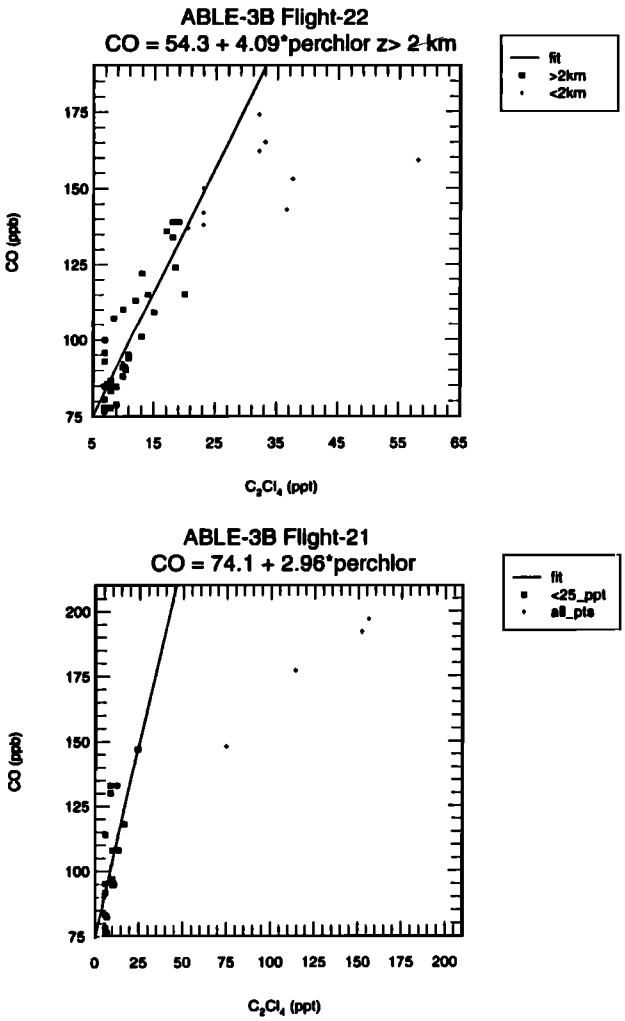

Fig. 2. Concentrations of C_2Cl_4 and CO observed over the East Coast of the United States (Maine - Virginia, flight 22): altitudes > 2 km, squares ; <2 km, pluses.

similar emission ratios as in North America and Canada (Table 2*a*), and emission inventories for both continents are consistent with observed atmospheric variance ratios (compare Tables 1 and 2*b*). The notable exception is $(CH_3)_2CO$, for which photooxidation of hydrocarbons dominates direct emissions [*Singh et al.*, this issue; see discussion below]. The consistency of observed enhancement ratios between flights and the harmony between emission inventories and ratios of concentration enhancements in the atmosphere provides evidence that the variance ratios in Table 1 are characteristic of industrial/urban sources.

Data for C_2H_6 and C_3H_8 over the United States show anomalies in which concentrations of both are markedly enhanced, without comparable elevation of CH_4 or other hydrocarbons (Figures 4*a*, 4*b*, 4*c*). A fuel source such as liquified petroleum gas (LPG) may be responsible. Long term measurements of hydrocarbons in rural New England also suggest disparate sources of C_2H_6 and C_3H_8, especially in winter when C_2H_6:C_2H_2 ratios are highly variable (A. H. Goldstein, private communication, 1993). Variance ratios of most other hydrocarbons are more uniform, relative to C_2H_2, in all seasons. Therefore in the present paper we use emission ratios from Table 1, relative to C_2Cl_4, neglecting anomalous points for C_2H_6 and C_3H_8. Thus we neglect these fuel-related sources and may slightly underestimate emissions of C_2H_6 and C_3H_8 from urban/industrial regions.

Characteristic Emission Ratios for Tundra/Taiga Fires Versus C_2H_2

Hydrocarbon emissions from biomass fires and ratios to CO and C_2H_2 are summarized in Table 3*a*, determined from haze layers with unperturbed halocarbon concentrations (flights 4, 6-9, 11; see Figure 5 for examples). Haze layers sampled on flights 18 and 19 (Table 3*a*, bottom panel) showed enhancements for long-lived species similar to those in flights 4, 6-9, and 11, but no enhancement of shorter-lived hydrocarbons. These haze layers had apparently aged long enough for short-lived species to be removed by photochemistry and for significant quantities of $(CH_3)_2CO$ to be generated.

The ratio C_2H_2:CO was remarkably consistent among flights (e.g., Figure 5). Hydrocarbon/CO ratios closely matched laboratory observations from smoldering combustion [*Lobert et al.*, 1991], as observed for Alaskan fire emissions [*Wofsy et al.*, 1992; *Blake et al.*, 1992]. With the notable exception of methane,

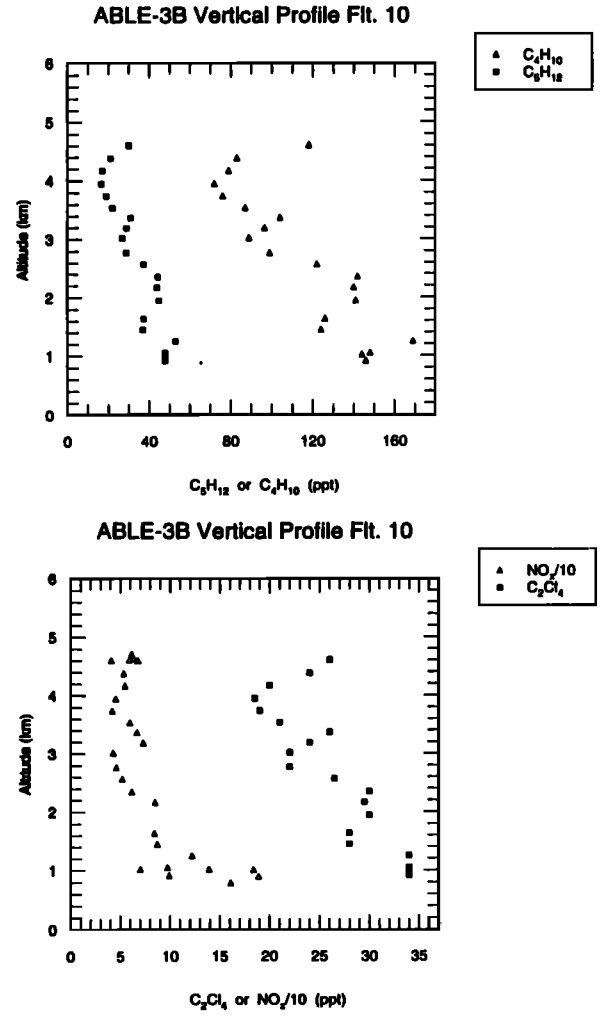

Fig. 3. (*a*) Vertical profiles of short-lived hydrocarbons (n–C_4H_{10}, C_5H_{12}) and (*b*) NO_x and C_2Cl_4 on flight 10. Strong inputs of short-lived species was reflected in enhanced concentrations relative to background levels, throughout the column 0-6 km. Largest enhancements were observed at the lowest altitudes, indicating rapid low-level advection of pollutants from source regions to the south.

TABLE 2*a*. Industrial/Urban Sources of C_2CL_4 and CO

	Region		
	USA+Canada	Europe (E+W)	Units
	Emission Rates		
C_2Cl_4[a]	154	293	kt/yr
CO[b]	77	161	Mt/yr
	Emission Ratios		
From inventories[a,b]	3000	3200	mol/mol
From ABLE3B data	3800	-	mol/mol

[a]*European Chlorinated Solvent Association* [1992]; P. Midgely (private communication, 1992).

[b]NAPAP, 1985; D. Jacob, J. Logan (private communication, 1992).

TABLE 2*b*. Anthropogenic Emission/Enhancement Ratios Relative to CO 10^{-3} mol/mol

Species	Emission Ratio NAPAP	Arctic Enhancement Table 1 (Range)
C_2H_2	3.6	2.4 (2-3.1)
C_2H_6	4.8	8.1 (3.7-30)
C_3H_8	4.5	2.6 (1.9-11)
$(CH_3)_2CO$	0.8	17.1 (12-23)

NAPAP, National Acid Precipitation Assessment Program.

emission ratios for most hydrocarbons are remarkably similar, relative to CO or C_2H_2, from biomass fires in a wide range of environments, including tundra, taiga, midlatitudes, and the tropics (see Table 3*b*). It appears that smoldering combustion provides the dominant source for emissions of these reduced gases, even though the fraction of fuel consumed in smoldering varies considerably, as indicated by the CO/CO_2 ratio [cf. *Laursen et al.*, 1992, *Lobert et al.*, 1991]. Emission ratios for methane are much higher in boreal fires than in fires at midlatitudes [*Laursen et al.*, 1992] or in the tropics [*Andreae et al.*, 1988], reflecting release of biogenic methane from peat soils in boreal wildfires (Table 3*b*). Emissions of NO_x are much lower than in most other biomass combustion or in pollution, reflecting the prevalence of smoldering combustion; the associated low NO_x/hydrocarbon ratio is responsible for the negligible rates of ozone photochemical production observed in boreal haze layers [*Jacob et al.*, 1992].

In the discussion below, we use concentrations of C_2H_2 and the ratios from Table 3a to assess hydrocarbon inputs from biomass fires. The relatively large emission ratios for $(CH_3)_2CO$ were taken from Table 3*b*, representing aged haze layers to account for secondary production from oxidation of labile olefins (e.g., propene). The observed variance ratio for C_2H_2:C_2Cl_4 from Table 1 was employed to account for input of C_2H_2 from by pollution sources (for flights with enhancements of C_2Cl_4). We selected C_2H_2 as the index species, instead of CO, to preserve correlations

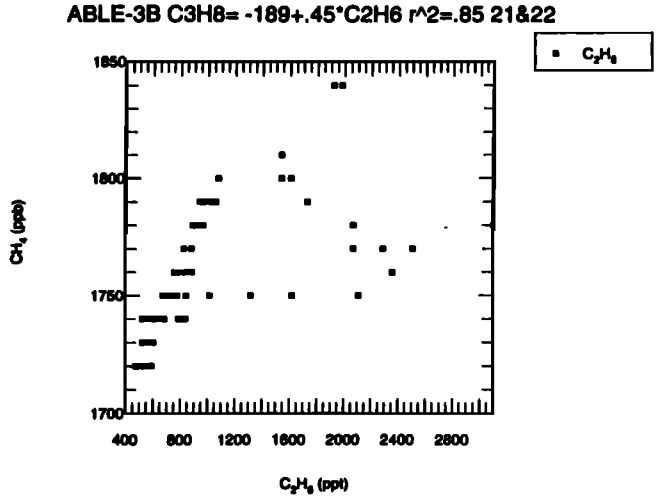

Fig. 4*a*. Relationships between concentrations of C_2H_6 and CH_4 over the East Coast of the United States, flights 21 and 22. Note the strongly deviant samples with greatly enhanced C_2H_6.

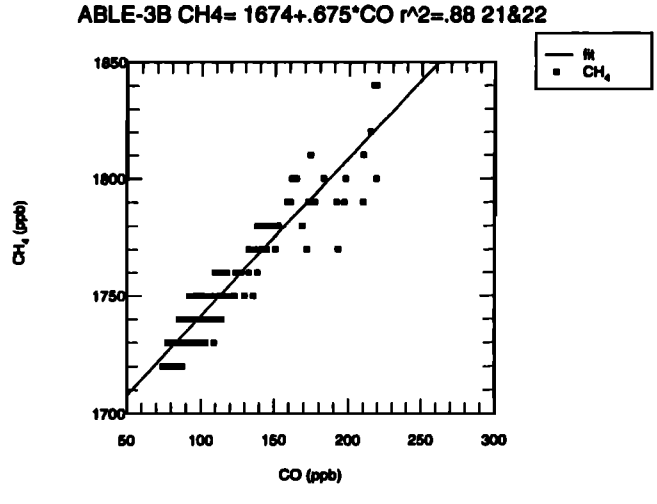

Fig. 4*b*. Relationships between concentrations of CO and CH_4 over the East Coast of the United States, flights 21 and 22. Note the absence of deviant samples evident in Figure 4*a*.

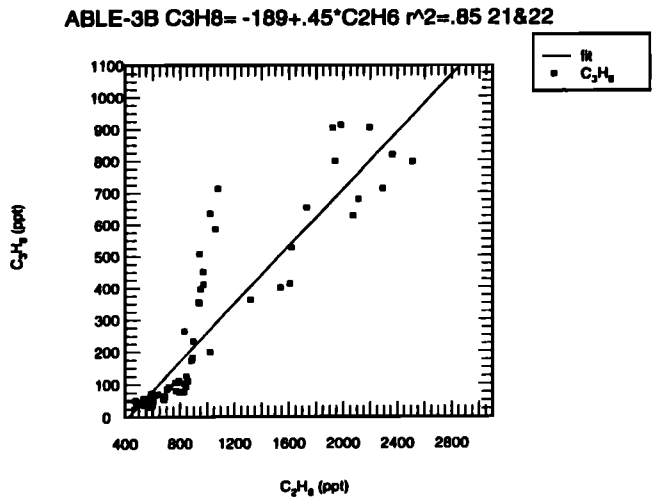

Fig. 4c. Relationships between concentrations of C_2H_6 and C_3H_8 over the East Coast of the United States, flights 21 and 22. The deviant samples with enhanced C_2H_6 (Figure 4a) are enhanced also in C_3H_8, consistent with a natural gas release.

among species from the grab samples. In all of the measurements reported here, in ABLE 3A [*Wofsy et al.*, 1992], and in Harvard Forest (A. H. Goldstein, private communication, 1993), CO and C_2H_2 are strongly correlated with uniform proportionality coefficient.

Background Concentrations

The background concentration is the characteristic value in the region, upon which anomalies reflecting local inputs or losses, or unusual transport events may be superimposed. The inputs, outputs, and chemical sources and sinks for a gas in a defined geographical region determine the regional budget. Both concepts are defined unambiguously for species with small spatial variance; neither is well defined for gases with short lifetimes and concentrated sources, since observed concentrations reflect particular circumstances of dilution, advection, and chemical reactions occurring after emission. The present analysis focuses

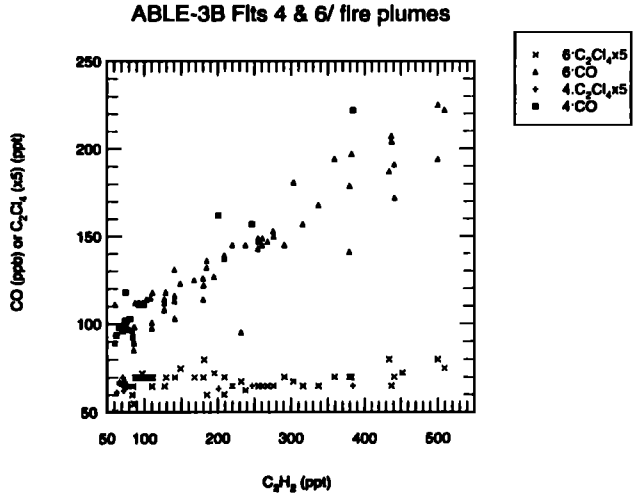

Fig. 5. Fire plumes observed on flights 4 and 6, showing strong correlations between C_2H_2 and CO, with no corresponding changes in C_2Cl_4. Symbols are: triangle, CO (flight 6); square, (flight 4); cross, C_2Cl_4 (x5 to expand the scale) (flight 6); plus, (flight. 4).

on gases with lifetimes of 1-12 weeks, long enough to establish a generally uniform background in the subarctic but short enough so that regional background concentrations are regulated significantly by chemical losses in the region.

Careful statistical analysis of observed concentrations is required in order to define regional background concentrations. For example, consider the cumulative distribution functions for CO and C_2H_2 concentrations on plotted in Figure 6a for flights 4-20. Here we employ probability axes, where normally distributed data fall on a straight line and $\pm 1\sigma$ corresponds to $\pm$ 1 quantile of standard normal. More than 50% of the CO observations lie within ±15% of the median, implying that the median of the aircraft observations represents a suitable background concentration. Anomalous high concentrations (> 1 standard quantile) represent primarily samples in haze layers.

For C_2H_2 (lifetime ~17 days), the cumulative probability plot is curved at the median (Figure 6a), a notably different distribution than for C_2H_2. Grab samples were acquired preferentially in haze layers, accounting for 40-50% of the samples, in contrast to the continuous measurements of CO, and the distribution reflects this bias. There may be a nonzero background concentration for n–C_4H_{10} (lifetime 5 days), but the median concentration for C_5H_{12} (lifetime 4 days) was ≈0 and the regional budget is evidently not well defined (Figure 6b).

Background concentrations for species measured in grab samples were derived by examining the subset of grab samples with corresponding CO concentrations within ±20% of median CO, exploiting the more representative sampling for CO. We adopted the trimmed mean (average excluding the highest and lowest 10%) of this subset to define background concentrations; other conditional selection procedures yielded indistinguishable results (Table 4). As expected, background concentrations were notably lower than means of all grab samples and slightly lower (5-10%) than corresponding medians.

Estimates for changes in background concentrations during the mission are needed for the budget analysis. Only a rough determination is possible due to the limited geographic area covered and the bias in selecting grab samples. Figure 7 shows the tenth percentile measurement for CO, C_2H_2, and C_2H_6 for each flight in the subarctic. Flight 10 sampled grossly polluted air, and flights 14-16 were affected by an unusual influx of tropical air [*Shipham et al.*, this issue; *Anderson et al.*, this issue; *Harriss et al.*, this issue, b]. Data for CO from flights 4-9 and 17-20 indicate a decline of 5-6 ppb during the 28 days of the mission, approximately the seasonal change expected for CO in the subarctic over the period (J. A. Logan, private communication, 1993). Even the 10th percentile of data from the smaller set of grab samples appears to be affected by biomass fires on Flights 6-9. We adopt the difference between flights 4 and 5 and 17-19 as an estimate of the change in background concentrations over the period; the corresponding rates of change ($(\Delta[i]_o/\Delta t)$ for species i) are shown in Table 5.

Figures 8 and 9 show meridional gradients for a variety of gases above the boundary layer (> 4 km) during transit flights on ABLE 3B and ABLE 3A, respectively. Concentrations of most species were higher in the subarctic than at midlatitudes during both missions for halocarbons and hydrocarbons but not for nitrogen oxides. This surprising result is consistent with the budget analysis given below. The latitudinal distribution for halocarbons indicates the influence of both European sources at high latitudes and inputs at midlatitudes from the United States. Boreal biomass fires provide a major source for hydrocarbons and PAN but have relatively little effect on NO_x or HNO_3 (Table 3).

TABLE 3*a*. Enhancement of Hydrocarbons Relative to CO from Boreal Biomass Burning

Flight	CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	i–C_4H_{10}	n–C_4H_{10}	n–C_5H_{12}	n–C_6H_{14}	C_6H_6	C_7H_8
						Fresh Haze Layers						
HBL												
04	0.65	2.35	8.38	5.40	1.83	1.30	0.09	0.43	0.21	0.15	1.67	0.77
06	.	3.70	5.08	6.49	.	1.87	0.07	0.31	0.12	0.09	1.57	0.57
07	.	3.44	7.96	6.17	0.82	1.49	0.07	0.45	0.21	0.12	1.81	0.78
08	0.42	2.29	1.02	6.36	0.28	2.55	.	.	.	.	1.16	0.30
09	0.30	2.49	0.61	6.91	.	2.06	0.25	0.63	0.21	.	1.03	.
LBQ												
11	0.32	2.58	0.92	5.85	.	2.34	0.32	0.67	0.20	0.06	1.04	.
Mean	0.42	2.81	.	6.20	.	1.94	.	0.50	0.19	.	1.38	.
±(1σ)	0.14	0.55	.	0.48	.	0.44	.	0.13	0.04	.	0.31	.
β	0.15	*1.00*	.	2.2	.	0.69	.	0.18	0.068	.	0.49	.
Flight	C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	i–C_4H_{10}	n–C_4H_{10}	n–C_5H_{12}	C_6H_6	C_7H_8	$(CH_3)_2CO$	
						Aged Haze Layers						
18	2.48	.	3.46	.	1.52	.	0.37	.	1.20	.	29	
19	2.00	.	4.40	.	1.74	.	0.51	.	0.65	.	26	

Haze layers with negligible enhancement of C_2Cl_4; HBL, Hudson Bay lowlands, Ontario; LBQ, Labrador and Quebec; aged haze layers are discussed by *Browell et al.* [1992] and *Blake et al.* [this issue]. Units, 10^{-3}mol/mol, except for CH_4 (mol/mol). Ratios not reported for correlation coefficients < 0.4. β, ratio to C_2H_2, used in Table 5. Means assumed ≈0 for short-lived, high-variance species.

REGIONAL BUDGETS OF TRACE SPECIES IN THE SUBARCTIC

The regional mass balance for C_2Cl_4, at latitudes > 56°N, may be derived by integrating the mass continuity equation over the volume of the subarctic region, the dividing by the volume to obtain an expression for the mean source of C_2Cl_4 in the region, $P_{ind}^{C_2Cl_4}$ (ppt/d),

$$P_{ind}^{C_2Cl_4} = [C_2Cl_4]_o k_{C_2Cl_4}[OH] + \frac{\Delta[C_2Cl_4]}{\tau_{ex}} + \frac{\Delta[C_2Cl_4]_o}{\Delta t} \quad (1)$$

where the terms on the right hand side represent regional photochemical loss, net exchange with midlatitudes, and concentration change during the observation period, respectively. Here $[C_2Cl_4]_o$ is the background concentration (cm^{-3}), $\Delta[C_2Cl_4]_o$ is the change during observation period Δt, $k_{C_2Cl_4}$ is the rate coefficient for reaction of OH with C_2Cl_4 ($1.3 \cdot 10^{-13} cm^3 sec^{-1}$), $\Delta[C_2Cl_4]$ is the concentration difference between 40 and 60°N latitudes, and τ_{ex} is the meridional exchange time (≈ 1 month according to *Crutzen and Gidel* [1983]). The 24-hour mean [OH] concentration during summer for latitudes > 56°N, altitudes 0-6

TABLE 3*b*. Comparison of ABLE 3B Enhancement Ratios (Versus CO) to Data From Other Experiments

	ABLE3A[a]			ABLE2B[b]	ABLE3B			Middle
Species	Tundra Fires	BERING Pollution	U.S. East Coast[c] Pollution	Amazon Fires	Taiga[d] Fires	Flight 21[e] Pollution	Flight 22[f] Pollution	Latitude Fire
CH_4	0.18	0.41	0.66	0.08	0.42	0.56	0.75	0.04
C_2H_2	0.0019	0.0020	0.0017	0.03	0.0028	0.0043	0.0028	0.0026
C_2H_4	NA	NA	NA	NA	--	0.0024	0.0005	NA
C_2H_6	0.0055	0.0096	0.04	0.007	0.0062	0.0040	0.0014	0.0061
C_3H_6	NA	NA	NA	NA	--	0.0002	0.0005	0.0066
C_3H_8	0.0008	0.0043	0.015	0.0014	0.0019	0.0047	0.0069	0.0023
n–C_4H_{10}	0.0001	0.0046	NA	NA	0.0005	0.0071	0.0032	0.0073
n–C_5H_{12}	NA	NA	NA	NA	0.00019	0.0020	0.0006	NA
C_6H_6	NA	NA	NA	NA	0.0014	0.0019	0.0010	NA
C_7H_8	NA	NA	NA	NA	--	0.0029	0.0006	NA
NO_y	0.0056	0.023	0.008	0.016	0.018	0.025	0.031	0.038
PAN	0.0017	NA	NA	NA	0.0036	0.0076	0.0057	NA

ABLE, Arctic Boundary Layer Expedition. Double hyphens denote insignificant correlation with CO; NA, species not measured.

[a] *Blake et al.* [1992]; *Harriss et al.* [1992]; *Wofsy et al.* [1992].

[b] *Andreae et al.*, 1988.

[c] Coastal Maine to Virginia, anthropogenic pollution.

[d] Flights 4,6,7,8,9,11: haze layers attributed to biomass burning, i.e., with insiginificant elevation of C_2Cl_4.

[e] Coastal Maine (pollution).

[f] Coastal Virginia (pollution). Forest and brush fires in the United States and Southern Canada, *Laursen et al.* [1992].

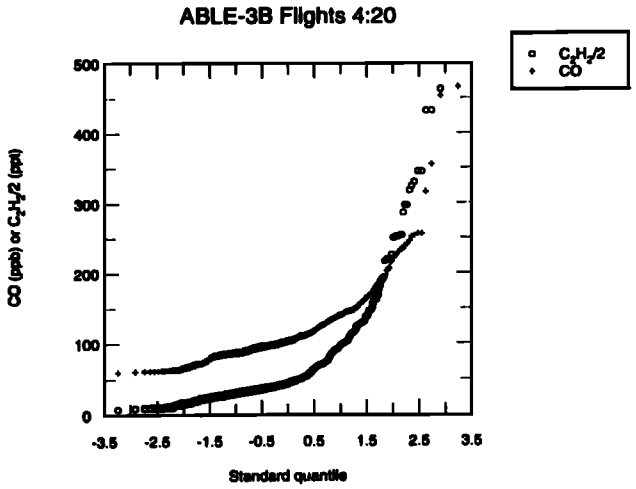

Fig. 6a. Cumulative probability distributions for CO (plus) and C_2H_2 (circle, scaled by 1/2), for flights 4-20 in ABLE 3B. The x-axis gives the quantiles of standard normal (±1 denotes ±1σ, ±2 denotes ±2σ, etc.), such that a Gaussian distribution plots as a straight line.

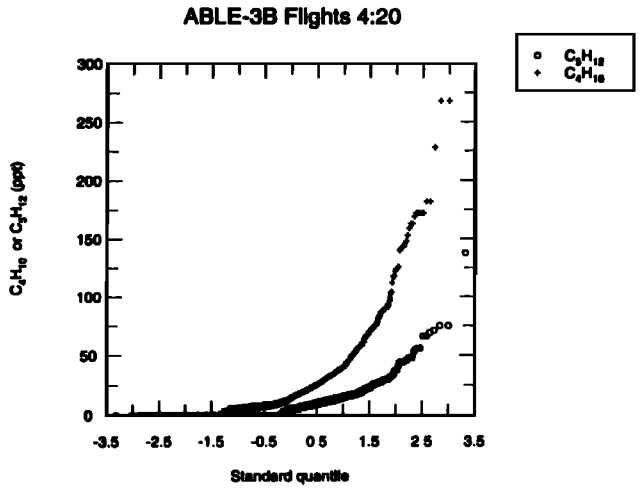

Fig. 6b. Same as Figure 6a, for n–C_4H_{10} (plus) and C_5H_{12} (circle) (ppt).

km, is $10^6 cm^{-3} s^{-1}$ according to model calcualtions [*Spivakovsky et al.*, 1990].

Table 5 shows our analysis of the budget for C_2Cl_4 for latitudes > 56°N. A mean input of 0.2 ppt/d is required to balance losses due to reaction with OH, transport to midlatitudes, and time dependence. This is equivalent to 120 kt/yr or about one fourth of European and North American emissions (Table 2a), a reasonable fraction since most European sources are located between 48° and 60°N, while most North American sources are south of 48°. Emission rates for C_2Cl_4 at high latitudes evidently exceed rates of consumption due to reaction with OH. The quantity of C_2Cl_4 exported from the subarctic cannot be determined accurately from our data due to the restricted spatial domain of the measurements, but the direction of net exchange is evident.

Table 5 summarizes regional inputs and losses for a number of species, given by

$$\alpha_i P_{ind}^{C_2Cl_4} + \beta_i P_{bb}^{C_2H_2} + P_{in\ situ} = [i]_o k_i [OH] + \frac{\Delta[i]}{\tau_{ex}} + \frac{\Delta[i]_o}{\Delta t} \quad (2)$$

where α_i is the mean variance ratio for pollutant i from Table 1; β_i is the mean variance ratio for i relative to C_2H_2 from Table 3; and $P_{in\ situ}$ represents production of oxidized species such as CO and $(CH_3)_2CO$ from photochemical degradation of hydrocarbon precursors. Photolysis provides an additional loss term in equation (2) for $(CH_3)_2CO$ (24-hour mean rate = 4.7×10^{-7} s^{-1} at 60°N, July 15, overhead O_3 column 330 Dobson Units (DU)).

The input of C_2H_2 from biomass fires, $P_{bb}^{C_2H_2}$ (= 3.8 ppt/d), was obtained by assuming balance in equation (2) for i = C_2H_2 (see Table 5). The source due to biomass fires is about twice as large as inputs from industrial/urban pollution. Since C_2H_2 has a shorter chemical lifetime than C_2Cl_4 (5 times faster reaction with OH), transport and time-dependence terms are considerably smaller for C_2H_2 than for C_2Cl_4, relative to regional chemical loss.

Discussion

Inputs of trace species to the region from biomass fires and pollution are computed in Table 5 using observed variances relative to C_2Cl_4 and C_2H_2, combined with budgets for C_2Cl_4 and C_2H_2 constructed above using model OH distributions [*Spivakovsky et al.*, 1990]. We can test how well the sources thus defined account for observed background concentrations by examining the ratio of terms on the right-hand side in equation (2)

TABLE 4. Background Concentrations Defined by Various Conditional Averages (Flights 4-20)

Species	Mean of all data	Median of all data	Median of 80<CO<120	Mean of 80<CO<120	Trimmed Mean 80<CO<120[a]
CO	110 ppb	102	99	99	99
CH_4	1751 ppb	1752	1750	1750	1749
C_2Cl_4	12 ppt	12	12	12	12
CH_3CCl_3	155 ppt	155	154	154	154
C_2H_6	807 ppt	758	738	759	745
C_3H_8	105 ppt	78	69	83	74
C_2H_2	126 ppt	86	80	93	83
C_6H_6	56 ppt	39	36	43	38
$(CH_3)_2CO$	1040 ppt	1214	1192	1147	1156
$CHCl_3$	5.1 ppt	5.1	5.1	5.2	5.0
F-113	79.2 ppt	79	79	79	79

[a]Mean of data between 10th and 90th percentiles for data selected as given for corresponding CO concentration (adopted as summertime background concentrations).

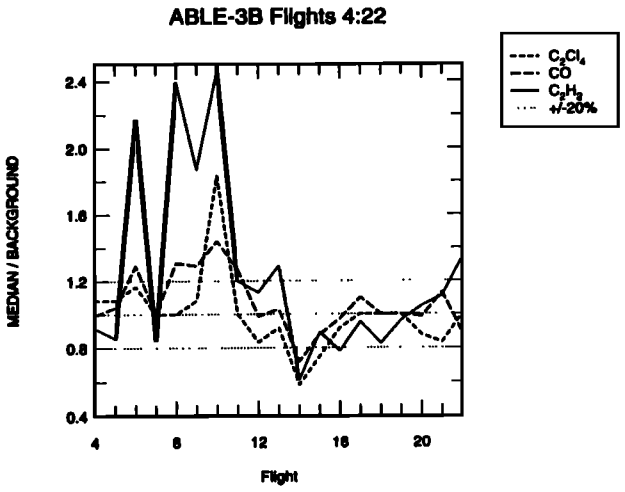

Fig. 7. Concentrations corresponding to the 10 th percentile, for each flight, for C_2H_2 (ppt), C_2H_6 (ppt, scaled by 0.05), and CO (ppb).

to terms on the left-hand side. The mean of these ratios (excluding C_2Cl_4 and C_2H_2), 0.8 (±0.2) (column 13 in Table 5), indicates remarkable consistency, with relative contributions of biomass fires and pollution defined to ±20%. The inferences drawn here about the relative contributions of industrial sources and biomass burning are relatively insensitive to the value adopted for [OH]: apart from usually small terms involving τ_{ex} and Δt, all the terms in equation (2) scale with [OH] ($[i]_0 k_i[OH]$, $P_{ind}^{C_2Cl_4}$ (equation (1)), and $P_{bb}^{C_2H_2}$, equation (2) with $i=C_2H_2$).

An independent check on the budget analysis is provided by comparing mean inputs from industrial/urban sources in Table 5 to the emission inventory in Table 2. The industrial source for CO to the subarctic corresponds to annual input of 85×10^6 t yr^{-1}, 36 % of North American and European sources. This appears to be a reasonable value in light of the geographic distribution of sources. Values for $\alpha_i P_{ind}^{C_2Cl_4}$ appear to correspond to similar fractions of emission inventories for hydrocarbons (Table 2*b*), except for $(CH_3)_2CO$ (see below).

The results in Table 5 show that biomass fires provide the dominant contribution to ambient background concentrations of many hydrocarbons in the boreal zone during summer. Biomass fires and methane oxidation are the principal sources of xxxx CO; there is a small additional source associated with oxidation of nonmethane hydrocarbons (Table 6*a*), mainly isoprene. Industrial/urban emissions play a smaller role, contributing 1/4 - 1/3 of total input (except 50% for n–C_4H_{10}). Rates for photochemical removal are larger than loss terms associated with time dependence or flux divergence, indicating that the composition of the atmosphere does not depend strongly on antecedent conditions or on exchange with lower latitudes.

We were surprised initially to observe consistent excess concentrations of trace species in the "clean" subarctic, as compared to midlatitudes, above the boundary layer. According to our analysis, this distribution reflects inputs from biomass fires that exceed the regional rate of scavenging by OH. Note that areas burned in the boreal zone in 1988 were about 2 times larger than in 1990 (Table 6*b*); the latitude gradient for CO was correspondingly larger (Figure 9), providing strong support for this analysis.

TABLE 5. Summertime Sources and Sinks for Hydrocarbons and CO in the Subarctic (ppt/d)

Gas	Concentration	OH Rate, cm^{-3} s^{-1}	τ_c, Days	Sinks $k_i[OH][i]$	Sinks hv	Time Dependence $\frac{\Delta[i]_0}{\Delta t}$	Transport $\frac{\Delta[i]}{\tau_{ex}}$	Sources $\alpha_i P_{ind}^{C_2Cl_4}$	Sources $\beta_i P_{bb}^{C_2H_2}$	Sources CH_4	Sources NMHCs	Sources/Sinks	Anthropogenic Fraction, %
C_2Cl_4	12 ppt	1.3×10^{-13}	89	0.13		-0.02	0.09	*0.20*	*0.*			*1.00*	*100*
C_2H_2	83 ppt	7.2×10^{-13}	16	5.2		-0.25	0.6	1.8	*3.8*			*1.00*	32
C_2H_6	745 ppt	2.2×10^{-13}	52	14.1		-3.5	5.5	3.4	8.4			0.73	29
C_3H_8	74 ppt	9.6×10^{-13}	12	6.1		-0.2	0.5	1.5	2.7			0.65	36
n–C_4H_{10}	8 ppt	2.3×10^{-12}	5	1.6		0.	0.17	0.74	0.7			0.81	51
C_6H_6	38 ppt	1.2×10^{-12}	9.6	3.9		-0.3	0.6	0.8	1.9			0.64	29
$(CH_3)_2CO$	1160 ppt	2.0×10^{-13}	15.7	20.0	54.1	ND[a]	8.3	13	46.6		5.9[b]	0.79	22
CO	105 ppb	2.2×10^{-13}	53	2000		-210	760	760	1330	680	227[c]	1.17	25

Numbers in italics denote balances assumed in the budget analysis; budget region 56°-90°N (1.1×10^{19} mol of air in the troposphere). ND, not determined. α, molar emission ratio relative to C_2Cl_4 from industrial pollution, Table 1; β, molar emission ratio relative to C_2H_2 from boreal biomass fires, Table 3; τ_c, chemical lifetime (days). Mean [OH], 1×10^6 cm^{-3} [*Spivakovsky et al.*, 1990] for July. Reaction rates (at 280°K), from *Atkinson* [1990]; $\Delta[i]/\tau_{ex}$, meridional exchange flux; τ_{ex}=30 days assumed; hv denotes photolysis; $(\Delta[i]/\Delta t)$ denotes the rate of change of background concentration from day 198→226 (28 days).

[a] No measurements were obtained on flights 1-13.

[b] Oxidation of C_3H_8 source in this column.

[c] Oxidation of isoprene provides 150 ppt/d, with the balance due to other nonmethane hydrocarbons.

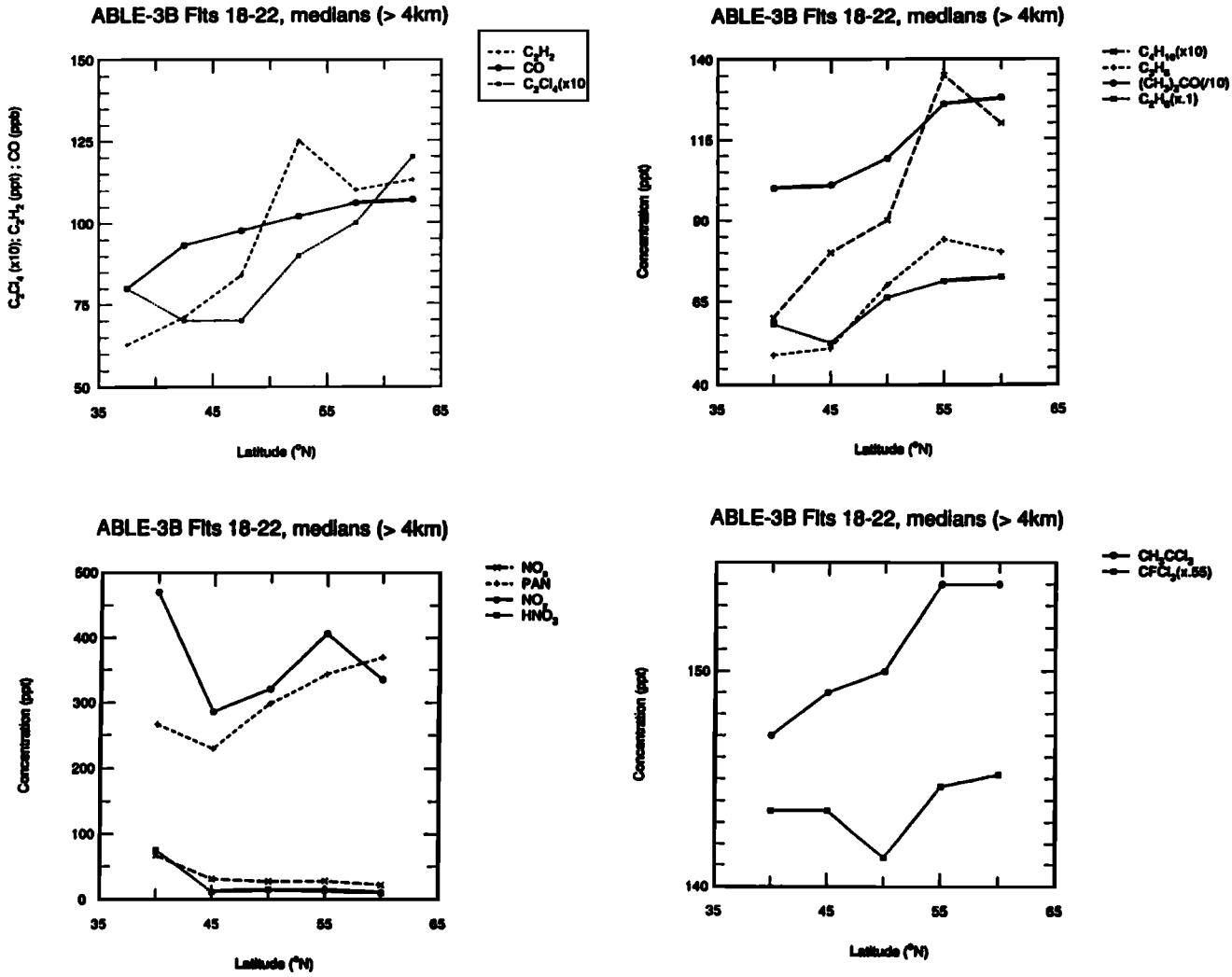

Fig. 8. Meridional distributions of median concentrations of trace gases above 4 km, for flights 18 - 22 in ABLE 3B, from Labrador to Virginia: (*a*) CO (ppb), C_2H_2 (ppt), and C_2Cl_4 (scaled ×10); (*b*) hydrocarbons (ppt), scaled as shown in the legend; (*c*) nitrogen oxides (ppt); and (*d*) long-lived halocarbons (ppt), scaled as shown in the legend.

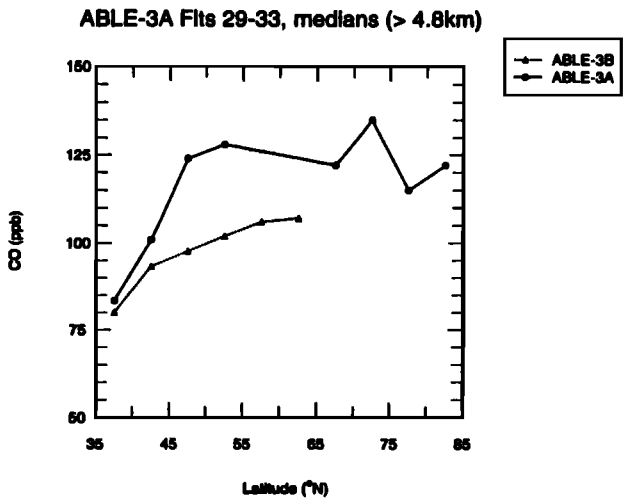

Fig. 9. Median concentrations in 5° latitude bins for CO (ppb): above 4 km, for flights 18 - 22 in ABLE 3B; above 4.8 km for flights 29 - 33 of ABLE 3A. These flights represent latitude transects along the East Coast of North America from Labrador to Virginia.

The global increase of CH_4 concentrations provides an important indirect human influence on CO concentrations. If two thirds of the source from CH_4 were attributed to anthropogenic increases, based on a preindustrial concentration of 0.6 ppm, the ratio of anthropogenic to natural inputs for CO would rise to about 0.6. The human influence might be higher if recent increases in areas burned annually [*van Wagner*, 1988] are associated with human activities. Hence CO concentrations appear to be strongly perturbed by global anthropogenic changes, even though direct pollution inputs are not large in the region during summer.

Acetone is a major source of acetylperoxy radicals, and it therefore plays an important role in producing PAN from NO_x. Direct industrial sources are small (Table 2), but observed variance ratios (Table 1) suggest much larger pollution sources. According to *Singh et al.* [this issue], most of the $(CH_3)_2CO$ associated with anthropogenic pollution arises from atmospheric oxidation of hydrocarbon precursors. Biomass fires provide a very strong source of $(CH_3)_2CO$ in the boreal zone (Table 3 and 5), likely due to secondary production from oxidation of the rich suite of reactive hydrocarbons produced in smoldering combustion

TABLE 6*a*. OH Removal and Atmospheric Production of CO in the Arctic 56°-90° N Latitude, Entire Tropospheric Column, July

Species	$\int \frac{[OH][X]k_X}{10^6} dz$ ($cm^{-2}s^{-1}$)	CO yield/ Carbon Atom	$\int \frac{P_{CO}}{10^6} dz$ ($cm^{-2}\ s^{-1}$)
C_2Cl_4	16	1	31
$CHCl_3$	4	1	4
C_2H_2	598	0.6	717
C_2H_6	1639	0.55	1803
C_3H_8	710	0.61	1300
$n\text{–}C_4H_{10}$	345	0.54	745
$i\text{–}C_4H_{10}$	132	0.72	380
$n\text{–}C_5H_{12}$	180	0.53	477
C_6H_6	456	0.09	81
C_7H_8	488	0.09	88
$(CH_3)_2CO$	2320	0.67	4663
Isoprene[a]	≈14600	1.15	≈16900
Total NMHC	21490	-	27190
CH_4	78750	1	78750
Total atmosphere	100240	-	106040
CO	220000	-	-

Yield of CO/molecule from *Altshuller* [1991].
[a]Mean isoprene emission rate, 50°-90°N (D. J. Jacob, private communication, 1992).

TABLE 6*b*. Annual Areas Burned in Canada

Year	Area (10^6ha)	Number of Fires
1988	1.36	10700
1990	0.93	10100
1981-90	2.1 (mean)	
1953-80	1.1 (mean)	
	0.5 (median)	

Stocks [1991]; B. Stocks, private communication, (1992).

[*Blake et al.*, this issue]. High $(CH_3)_2CO$ concentrations associated with biomass fires could play a crucial role in regional NO_x chemistry [*Jacob et al.*, 1992; *Singh et al.*, 1992], promoting preservation of reactive nitrogen as PAN over oxidation to rapidly deposited HNO_3.

CONCLUSION

Biomass fires represent major sources for nonmethane hydrocarbons, CO, and $(CH_3)_2CO$ in the subarctic during summer. Long-range transport of pollution, apparently originating primarily from high-latitude European sources, provides 1/3 - 1/4 of the total input to the region. Emissions of hydrocarbons, CO, and C_2Cl_4, from wildfires and industrial sources, exceed the rates for removal by reaction with OH, and the "clean" subarctic represents a net source of these species to midlatitudes.

The dominant role of emissions from biomass fires implies that regional concentrations for many gases should respond to variations in areas burned during the summer, a view supported by comparison of CO data from 1988 and 1990. Assessments of global environmental change should recognize the pervasive influence of biomass fires in the boreal zone and take into account long-term trends in fire frequency [*van Wagner*, 1988], which may be connected to climate warming [*Schindler et al.*, 1990], increased population, or other global phenomena.

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